

UNITED STATES PATENT OFFICE

2,476,008

**p-HYDROXY BENZYL ALCOHOL COUPLERS
FOR COLOR PHOTOGRAPHY**

Paul W. Vittum and Arnold Weissberger, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester N. Y., a corporation of New Jersey

No Drawing. Application September 28, 1945,
Serial No. 619,261

10 Claims. (Cl. 95—6)

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This invention relates to photographic color-forming or coupling compounds and particularly to color-forming compounds of the p-hydroxy benzyl alcohol class.

The formation of colored photographic images by using a primary aromatic amino developing agent which couples with a color-forming compound on development has been the subject of numerous prior patents. Most of these patents have been directed to coupler compounds which produce on development dyes which meet the requirements of subtractive color photography, that is, dyes which are colored yellow, magenta or cyan. The phenolic couplers generally produce cyan dyes and the present invention relates to couplers of this type.

It has heretofore generally been supposed that phenolic couplers in order to be active in the coupling reaction should have either a hydrogen atom or a so-called readily replaceable group such as halogen or sulfonic acid in the position in the phenolic ring rendered reactive by the phenolic hydroxyl group. The reactive position is generally para to the phenolic hydroxyl group except with β -naphthol derivatives, where the 1-position is reactive.

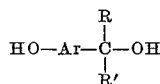
Where the coupler compound is incorporated in the sensitive emulsion layer or multi-layer systems, the coupler molecule is generally made of such size and configuration that there is no diffusion in the gelatin or other colloidal carrier for the silver halide. Upon coupling with the development product of the developing agent, the configuration of the coupler is usually retained in the coupled dye and this dye is at least as complex in configuration as the original coupler. This is not always a desirable condition as will be pointed out in detail hereinafter.

It is therefore an object of the present invention to provide novel coupler compounds for color photography. A further object is to provide phenolic coupler compounds which possess substituent groups in the reactive position of the phenol ring, said groups not usually considered to be replaceable in the coupling reaction. A still further object is to provide coupler compounds which upon coupling produce a dye of relatively simple structure. Other objects will appear from the following description of our invention.

These objects are accomplished by the use as coupler compounds of p-hydroxy benzyl al-

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cohols and their derivatives of the following general structure:



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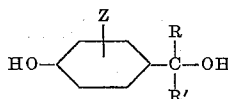
in which R and R' represent hydrogen or substituents such as halogen or hydrocarbon which may or may not be substituted, R and R' being the same or different, and Ar represents an arylene radical to which the hydroxyl group and the carbon atom are attached in para position.

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More specifically, we have found that phenolic compounds of the following structure are useful

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couplers for color photography



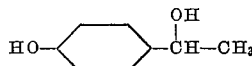
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in which R and R' are the same as before and Z and Z' are hydrogen or substituents such as halogen, hydrocarbon, alkoxy, amino or substituted amino groups, carboxy or fused-on ring systems as in the case of naphthols.

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The following compounds illustrate couplers of this class:

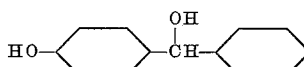
1.



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Methyl p-hydroxyphenyl carbinol

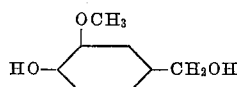
2.



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p-Hydroxybenzhydrol (Ann., 210, 253)

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3-methoxy-4-hydroxybenzyl alcohol (vanillyl alcohol) (Ber., 27, 2411)

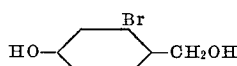
4.



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p-Hydroxybenzyl alcohol (Ber., 32, 3374)

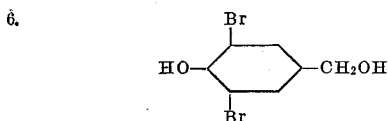
5.



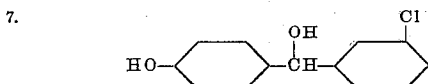
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2 - bromo - 4 - hydroxybenzyl alcohol (Ann., 334, 330)

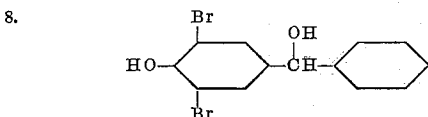
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3,5 - dibromo - 4 - hydroxybenzyl alcohol (Ber., 32, 3377)



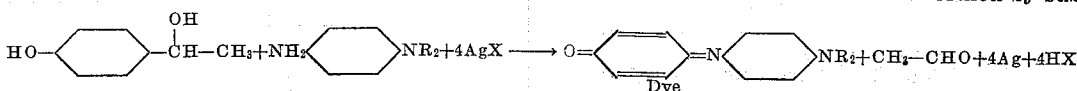
4-hydroxy-3'-chlorobenzhydryl (Ber., 39, 1936)



3,5 - dibromo - 4 - hydroxybenzhydryl (Ann., 334, 379)

Many other compounds with varying types and arrangements of substituents are possible and fall within the scope of our invention.

It will be seen that the couplers of our invention all have a group not usually considered to be a replaceable group, in the reactive position of the phenolic ring. However, our couplers are very reactive in the coupling reaction and we believe that in this reaction the couplers are split between the phenolic nuclei and the central carbon atom. For example, methyl p-hydroxyphenyl carbinol has been found to produce the same dye as is formed by phenol itself. Thus with coupler No. 1, methyl p-hydroxyphenyl carbinol, the dye-forming process may be represented by the following equation:



In this equation R represents an alkyl or substituted alkyl substituent in the developer and X represents halogen. The equation shows that an aldehyde, in this case acetaldehyde, is released and the usefulness of this compound will be pointed out more fully hereinafter.

Because the coupling reaction of our couplers involve this splitting our couplers can be used advantageously in those processes where it is desired to produce relatively simple dyes from larger coupler molecules. We believe that much of the graininess of color photography obtained by coupling those color-forming compounds which are incorporated in the sensitive emulsion and are non-diffusing in the gelatin, is due to the fact that the coupled dye is incapable of any diffusion in the emulsion. A small degree of diffusion appears to be desirable and our couplers enable this to be achieved because the coupler molecule is split during the coupling and the final dye is a relatively simple molecule as compared with the dye which would be obtained if the coupler molecule were not split in this way.

A further advantage in our couplers is that the splitting brought about by the coupling releases an aldehyde. This is illustrated in the equation above for the coupler methyl p-hydroxyphenyl carbinol. In this case the aldehyde is acetaldehyde and corresponding aldehydes are released in the case of other couplers. This aldehyde released at the point of coupling exerts a tanning action on the gelatin and therefore tends to decrease graininess of the resulting image.

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The ordinary coupling reaction is often accomplished by a melting of the gelatin in the vicinity of the individual grains. This melting is caused by a combination of facts such as local high bromide liberation, local heat liberation, etc. By releasing a tanning agent at the point of coupler, this emulsion melting is overcome to a large extent and the graininess of the resulting dye image is reduced.

The following example illustrates a developing solution containing one of the couplers of our invention.

(a) 2-amino-5-diethyl-amino-hydrochloride (HCl)	grams	2
Sodium sulfite	do.	5
Sodium carbonate	do.	30
Water to	liter	1
(b) Methyl p-hydroxyphenyl carbinol	grams	2
Sodium hydroxide (10% solution)	cc.	10

In use, (b) is added to (a).

In addition to their use in the developing solution, the coupler compounds of our invention may be incorporated in the photographic layer prior to exposure and the colored images formed by development in primary aromatic amino developing solution.

Our couplers may be incorporated in emulsions in the manner described in Mannes and Godowsky U. S. Patent 2,304,940, granted December 15, 1942, or Jelley and Vittum 2,322,027 granted June 16, 1943.

The aromatic amino developing agents used with the coupling compounds of our invention include the mono-, di- and tri-amino aryl compounds and their derivatives formed by substitu-

tion in the amino group as well as in the ring such as alkyl phenylene diamines and alkyl toluylene diamines. These compounds are usually employed in the salt formed such as the hydrochloride or the sulfate which is more stable than the amines themselves. Suitable compounds are diethyl p-phenylene - diamine hydrochloride, monomethyl p-phenylenediamine hydrochloride and dimethyl p-phenylenediamine sulfate. The p-aminophenols and their substitution products may also be used where the amino group is unsubstituted. All of these developing agents have a unsubstituted amino group in which the oxidation products of the developer couple with the color-forming compounds to form dye images.

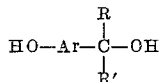
Our couplers may be employed for the production of colored photographic images in layers of gelatin or other carrier such as collodion, organic esters of cellulose or synthetic resins. The carrier may be supported by a transparent material such as glass, cellulose ester or a non-transparent reflecting medium such as paper or an opaque cellulose ester. The emulsion may be coated as a single layer or as multiple layers on the support or in the case of a transparent support as superposed layers on one or both sides of the support. The superposed layers may be differentially sensitized for the production of natural colored images in a well-known manner.

The examples and compounds set forth herein are illustrative only and it will be understood that our invention is to be taken as limited only by the scope of the appended claims.

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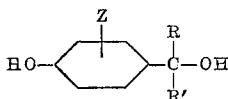
We claim:

1. The method of producing a colored photographic image in a gelatino silver halide emulsion layer which comprises exposing said emulsion and developing it with a primary aromatic amino developing agent in the presence of a coupler compound of the general formula:



where R and R' are selected from the class consisting of hydrogen, hydrocarbon and heterocyclic groups and Ar is an arylene radical to which the hydroxyl group and the carbon atom are attached in para-position.

2. The method of producing a colored photographic image in a gelatino silver halide emulsion layer which comprises exposing said emulsion and developing it with a primary aromatic amino developing agent in the presence of a coupler compound of the general formula:



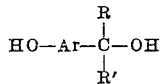
where R and R' are selected from the class consisting of hydrogen, hydrocarbon and heterocyclic groups and Z is selected from the class consisting of hydrogen, halogen, hydrocarbon, alkoxy, carbethoxy, amino and fused-on aromatic ring.

3. The method of producing a colored photographic image in a gelatino silver halide emulsion layer which comprises exposing said emulsion and developing it with a primary aromatic amino developing agent in the presence of methyl p-hydroxyphenyl carbinol.

4. The method of producing a colored photographic image in a gelatino silver halide emulsion layer which comprises exposing said emulsion and developing it with a primary aromatic amino developing agent in the presence of p-hydroxybenzhydrol.

5. The method of producing a colored photographic image in a gelatino silver halide emulsion layer which comprises exposing said emulsion and developing it with a primary aromatic amino developing agent in the presence of 3,5-dibromo-4-hydroxy-benzyl alcohol.

6. A color-forming photographic developer comprising a primary aromatic amino developing agent and a coupler compound having the general formula:

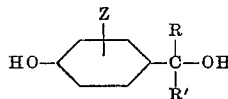


where R and R' are selected from the class consisting of hydrogen, hydrocarbon and heterocyclic groups and Ar is an arylene radical to which the hydroxyl group and the carbon atom are attached in para-position.

7. A color-forming photographic developer comprising a primary aromatic amino developing

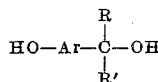
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agent and a coupler compound having the general formula:



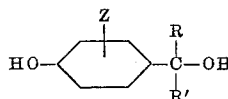
where R and R' are selected from the class consisting of hydrogen, hydrocarbon and heterocyclic groups and Z is selected from the class consisting of hydrogen, halogen, hydrocarbon, alkoxy, carbethoxy, amino and fused-on aromatic ring.

8. A photographic emulsion for forming colored images comprising a water-permeable carrier containing a sensitive silver halide and a coupler compound having the general formula:



where R and R' are selected from the class consisting of hydrogen, hydrocarbon and heterocyclic groups and Ar is an arylene radical to which the hydroxyl group and the carbon atom are attached in para-position.

9. A photographic emulsion for forming colored images comprising a gelatino silver halide emulsion containing a coupler compound having the general formula:



where R and R' are selected from the class consisting of hydrogen, hydrocarbon and heterocyclic groups and Z is selected from the class consisting of hydrogen, halogen, hydrocarbon, alkoxy, carbethoxy, amino and fused-on aromatic ring.

10. The method of developing a colored image in a gelatino-silver halide emulsion and simultaneously tanning the gelatin in the region of the developed image which comprises developing said emulsion with a primary aromatic amino developing agent in the presence of a phenolic coupling compound having in the reactive position para to the phenolic hydroxyl group an aliphatic alcohol radical which splits off from the coupler to form an aldehyde and to tan the gelatin during coupling.

PAUL W. VITTUM.
ARNOLD WEISSBERGER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,197,311	Merckx et al.	Apr. 16, 1940

FOREIGN PATENTS

Number	Country	Date
836,144	France	Oct. 10, 1938
506,224	Great Britain	May 24, 1939